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Synthesising a polysilane

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SYNTHESISING A POLYSILANE

This invention relates to a method of synthesising an unsubstituted polysilane, having an approximate composition of $(\text{SiH}_n)_x$ where x is large (such as at least 10) and n is from 1 to 2.

Unsubstituted polysilanes are potential precursors for hydrogenated amorphous silicon films. These films have properties such as photoconductivity and could be used in xerography, image intensifiers and photovoltaic devices including solar cells, which may comprise films of such amorphous silicon on substrates. Such solar cells promise to offer the important advantage of moderate cost for large areas at reasonable efficiencies.

Various syntheses for polysilanes are already known. Some have as their starting material such compounds as $(\text{SiBr}_2)_x$ or Si_5H_{10} , which are not commercially available, thus adding to the number of steps necessary. Another has as its starting material SiHBr_3 , which as generally prepared is said to be explosive. A typical known synthesis, reported by Stock and Zaidler in Berichte, 56B(1923)986, is

$\text{SiHCl}_3 + \text{Na} \rightarrow (\text{SiH})_x$
but as the sodium is in the form of amalgam, separation of the product is difficult.

Another typical known synthesis, reported by Stock and Somieski in Berichte, 56(1923)247, is

$\text{SiH}_3\text{Cl} + \text{Na} \rightarrow (\text{SiH}_2)_x$
but the yield is small (theoretical maximum $2/3x$), the principal product being monosilane, which can explode on contact with air.

Another synthesis, but intending to lead to a variety of substituted ring compounds, is reported by Matsumura, Brough and West in JCS Chemical Communications 1978 p1092:

$\text{Si}(\text{CH}_3)_2\text{Cl}_2 + \text{Li}(\text{tetrahydrofuran}) \rightarrow (\text{CH}_3)_2\text{Si}_x + 54\text{H}_2$
ring compounds.

According to our invention, a method of synthesising an unsubstituted polysilane (of approximate composition $(\text{SiH}_n)_x$)

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having the repeating unit $-\text{SiH}_m-$ where n is from 1 to 2, comprises reacting $\text{SiH}_m\text{X}_{4-m}$ where X is fluorine, chlorine, bromine or iodine and $m = 1, 2$ or 3 , with lithium in a suspension of liquid inert to the reagents and the product and in which the polysilane is insoluble.

05 X is preferably chlorine. Writing the unsubstituted polysilane as $(\text{SiH}_m)_x$, x is preferably at least 10. m is preferably 1 or 2, particularly 2.

The molar ratio of lithium: $\text{SiH}_m\text{X}_{4-m}$ should preferably exceed $(4 - m):1$ and is more preferably at least $2\frac{1}{2}(4 - m):1$ (i.e. 5:1 for 10 dihalosilane). The weight ratio of the lithium to the liquid may be for example 1:90.

The liquid is preferably one in which the LiX also produced is soluble, and is preferably present in an amount sufficient to dissolve all the LiX that will be produced. A suitable liquid is 15 tetrahydrofuran.

The invention will now be described by way of example.

EXAMPLE 1

Lithium (0.3g; 0.04 mol) was suspended in 30 cm³ (27g) 20 rigorously dried and degassed tetrahydrofuran. This was reacted in the absence of moisture and air with gaseous dichlorosilane SiH_2Cl_2 (0.20g; 0.002 mol, initial partial pressure at room temperature 400 torr.)

An orange air-sensitive powder eventually precipitated (in our 25 case after 18 hours) and was removed from the suspension in not more than 24 hours in order to minimise further reaction of the powder. The powder fell to the bottom while the lithium tended to remain at the top; this aided separation. The tetrahydrofuran when subsequently exposed to air showed no reactivity, and this 30 implies that silane ring compounds (which would be soluble in tetrahydrofuran) were not formed to any significant extent. Also the lithium chloride which is produced in the reaction and which dissolves in the tetrahydrofuran could be precipitated from the latter by adding hexane to the tetrahydrofuran.

35 The orange powder was found by infrared spectroscopy to show spectral features closely analogous to thin films of hydrogenated

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amorphous silicon prepared by glow discharge techniques. The powder is thus considered to be unsubstituted polysilane, of composition $(SiH_n)_x$ where n is approximately 2; x (from other evidence) appeared to be at least 20.

EXAMPLE 2.

Lithium (0.3g; 0.04 mol) was suspended in 30 cm³ (27g) rigorously dried and degassed tetrahydrofuran. This was reacted in the absence of moisture and air with liquid trichlorosilane $SiHCl_3$ (0.27g; 0.002 mol) at room temperature. The trichlorosilane appeared to be miscible with the tetrahydrofuran.

A brown air-sensitive solid powder eventually precipitated (in our case after 18 hours) and was removed from the suspension in not more than 24 hours in order to minimise further reaction of the powder. The powder fell to the bottom while the lithium tended to remain at the top; this aided separation. The tetrahydrofuran when subsequently exposed to air showed no reactivity, and this implies that silane ring compounds (which would be soluble in tetrahydrofuran) were not formed to any significant extent.

From infrared spectroscopy, the brown powder is considered to be unsubstituted polysilane, of composition $(SiH_n)_x$ where n is approximately 1. From other evidence, x appeared to be 20 or more.

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CLAIMS

1. A method of synthesising an unsubstituted polysilane, having the repeating unit $-\text{SiH}_n-$ where n is from 1 to 2,
comprising reacting $\text{SiH}_m\text{X}_{4-m}$, where X is fluorine,
chlorine, bromine or iodine and $m = 1, 2$ or 3 , with lithium in a
5 suspension of liquid inert to the reagents and the product and in
which the polysilane is insoluble.
2. A method according to Claim 1, wherein the unsubstituted polysilane
being written as $(\text{SiH}_n)_x$, x is at least 10.
3. A method according to Claim 1 or 2, wherein X is chlorine.
- 10 4. A method according to any preceding claim, wherein m is 1 or 2.
5. A method according to Claim 4, wherein m is 2.
6. A method according to any preceding claim, wherein the liquid
is one in which the LiX also produced is soluble.
7. A method according to Claim 6, wherein the liquid is
15 tetrahydrofuran.
8. A method according to Claim 6 or 7, wherein the liquid is
present in an amount sufficient to dissolve all the LiX that will
be produced.
9. A method of synthesising a polysilane substantially as herein-
20 before described with reference to Example 1 or Example 2.
10. A polysilane which has been synthesised, by the method of any
preceding claim.

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